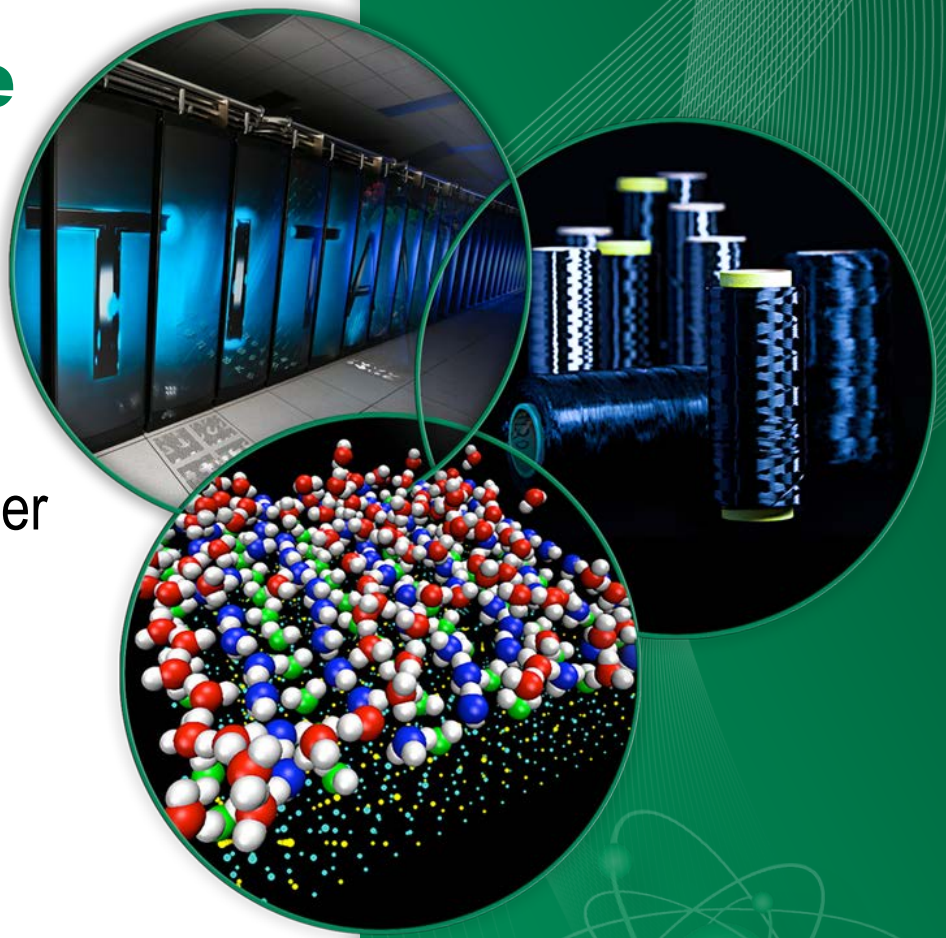
Lithium-Bearing Mixed Polyanion (LBMP) Glasses as Cathode Materials



Project ID: ES184

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Presenter: Andrew Kercher

Oak Ridge National Laboratory

DOE Annual Merit Review

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Overview

Timeline

- Start date: June 22nd, 2012
- End date: Sept. 30th, 2015
- Percent complete: 27%

Budget

- Total funding: $1.42M
  - DOE share: $1.42M
- Funding received in FY2012: $335K
- Funding for FY2013 (est.): $300K

Barriers

- Higher energy densities (350 Wh/kg cell*)
  - Est. cathode energy densities up to >1000 Wh/kg
- Excellent cycle life (PHEV 3-5K deep discharges*)
  - Rigid covalent structure and no irreversible phase changes
- Cost (PHEV $300/kWh*)
  - Commercial, non-exotic processing methods

*VT Program Multi-Year Plan values

Partners

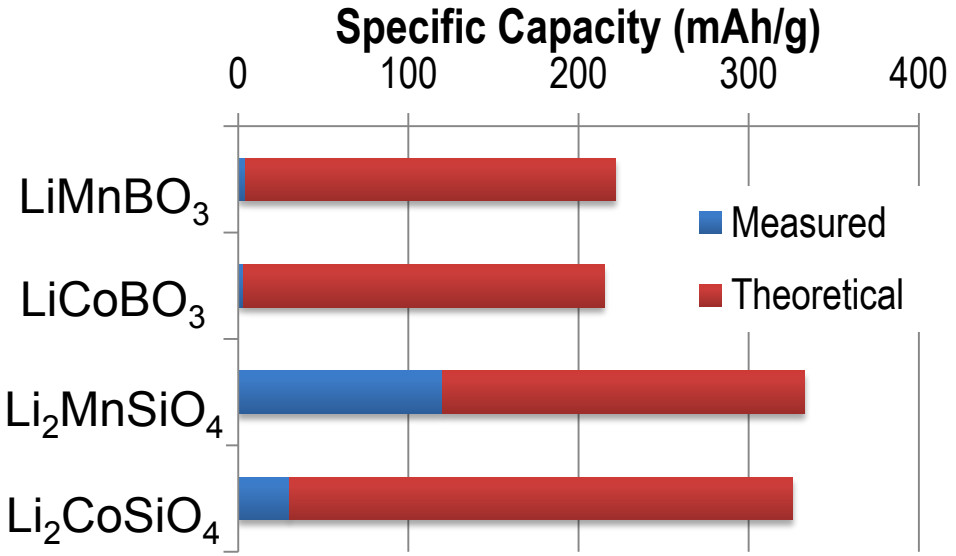
- Collaborations with ORNL glass processing specialists
  - Lynn Boatner, Joanne Ramey, Pooran Joshi
- Discussions of potential collaborations with BATT program members
  - Vince Battaglia (LBNL), Brett Lucht (Univ. of R.I.)

Mixed polyanion glasses could succeed where other crystalline cathode materials have failed

Relevance

- Several highly promising polyanionic crystalline cathodes have failed due to poor electrical conductivity or irreversible phase transformations.

Mixed polyanion glass cathodes offer the potential of achieving the excellent theoretical specific energies of promising crystalline framework materials.



- Mixed polyanion glasses can have electrical conductivities orders of magnitude higher than similar polyanionic crystalline materials.[1,2,3,4]
- During lithium cycling, glasses will not undergo irreversible phase transformations like crystalline materials.[5,6,7]

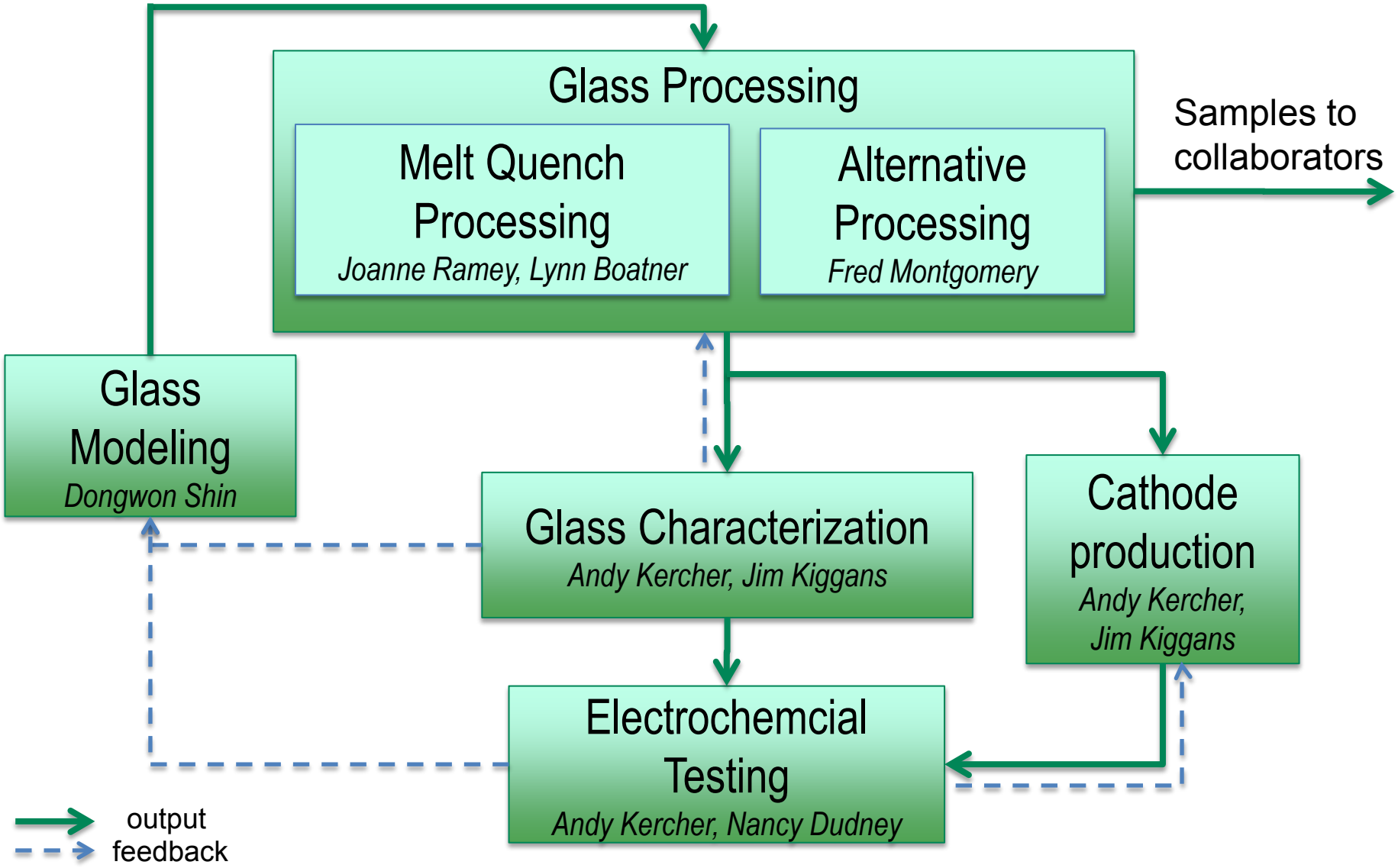
1. Mogus-Milankovic M, et al., 2004.
2. Tanaka K, et al.,1990.
3. Shapaan M, et al., 2009.
4. Santic B, et al., 2001.
5. Legagneur V, et al., 2001.
6. Domiko R, et al., 2007.
7. Lyness C, et al., 2007.

Fiscal year objectives

- To demonstrate proof-of-principle for the concept of mixed polyanion glass cathodes
- To produce mixed polyanion glasses based on crystalline phosphate materials
- To predict the electrochemical performance of polyanion glasses using computational thermodynamic modeling

Iron phosphate glass for battery cathodes, as cast

Program structure



Milestones

FY2012

Due Date	Description	Status
Sept. 30, 2012	Synthesize and characterize one baseline glass cathode composition.	Complete
Dec. 31, 2012	Synthesize, characterize, and perform electrochemical testing on two baseline glass cathode compositions.	Complete
Dec. 31, 2012	Create CALPHAD thermodynamic database for the baseline system.	Complete

FY2013

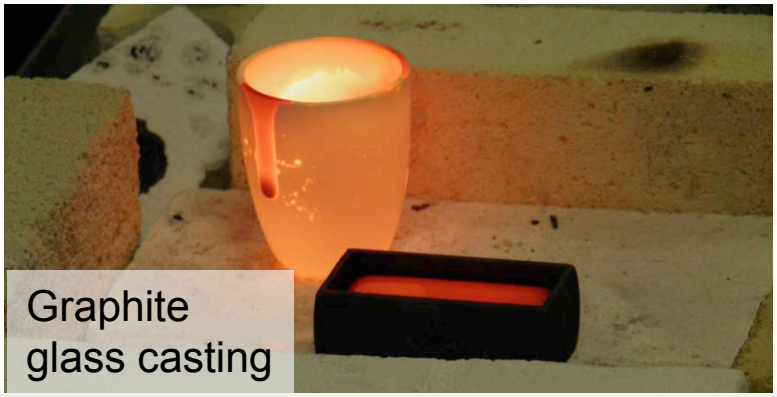
Due Date	Description	Status
Jan. 31, 2013	Setup CALPHAD database and perform initial simulation for one glass composition.	Complete
Sept. 30, 2013	Synthesize, characterize, and perform electrochemical testing on at least four different glass compositions.	On schedule
Sept. 30, 2013	Create CALPHAD thermodynamic database and verify results with comparison to initial experimental glass compositions and electrochemical performance.	On schedule

Production of polyanion glass cathode materials

Technical Accomplishments

- Initial focus was placed on producing iron phosphate / vanadate glass cathode materials by conventional glass processing in air.
- Produced, characterized, & battery tested 2 baseline iron phosphate glasses and 2 mixed polyanion glasses:

Baseline glass	Mixed Polyanion Glasses	similar crystalline cathode material
$0.9\ Fe_2O_3 \bullet 1\ P_2O_5$	--	$LiFePO_4$
$Fe_4(P_2O_7)_3$	$Fe_4(70\%\ P_2O_7\ ,\ 30\%\ V_2O_7)_3$ $Fe_4(50\%\ P_2O_7\ ,\ 50\%\ V_2O_7)_3$	$Li_4Fe_4(P_2O_7)_3$



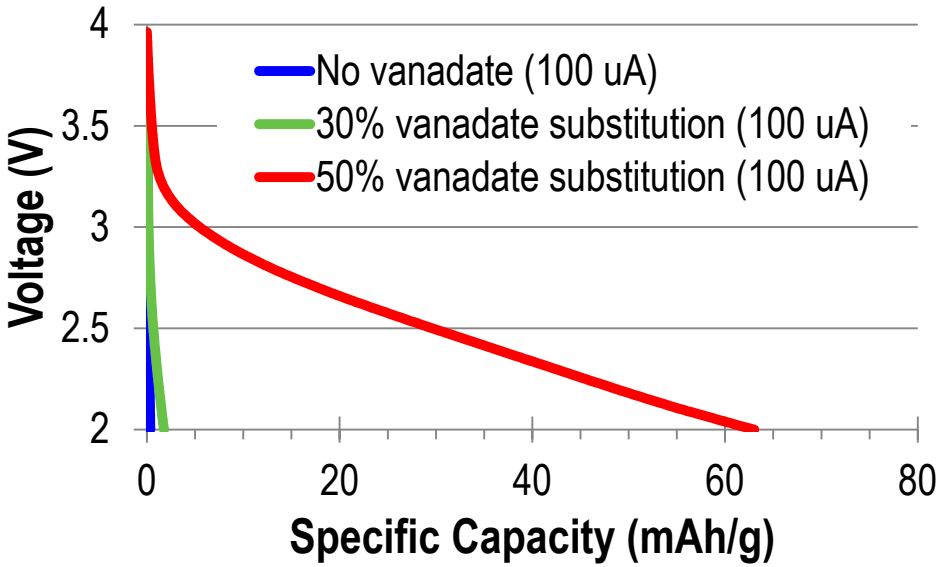
Graphite glass casting

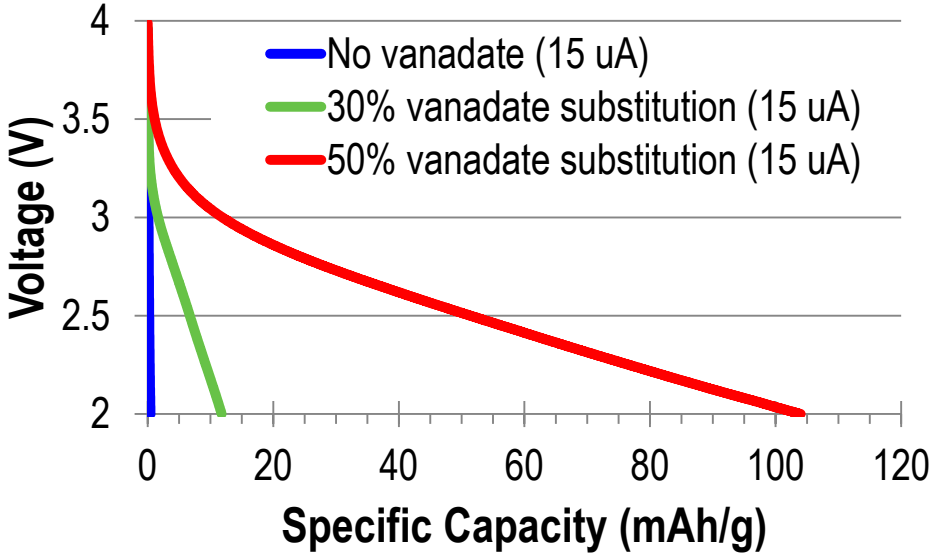
Splat quenching

Battery testing of polyanion glasses

Technical Accomplishments

- The effect of vanadate substitution in the glass on electrochemical performance was explored for the $Fe_4(P_2O_7)_3$ material.
- Coin cell testing
- Slurry contains glass, PVDF, and carbon black
  - 3-6 μm particle size
  - revised carbon black content in slurry for 50% substituted glass (change from 10 wt.% to 30 wt.%)
- The change in performance is primarily due to glass composition.



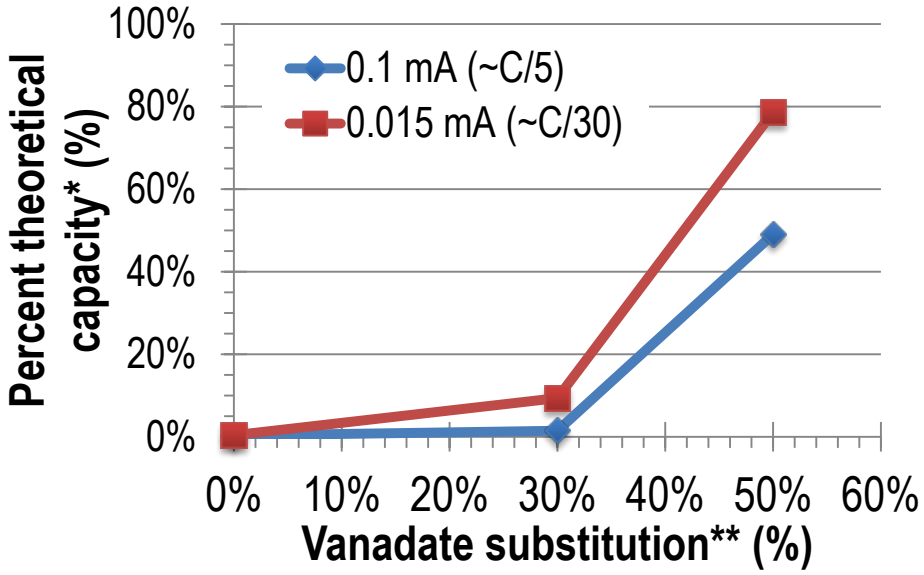


Improved performance in mixed polyanion glasses

Technical Accomplishments

- Proof-of-principle: The rate performance and specific capacity has been shown to improve with the substitution of vanadate polyanions.
- Glass characterization and literature data suggest that a significant percentage of Fe^{2+} is present in the glass, which reduces the maximum capacity.

A mixed polyanion glass was shown to have better electrochemical performance than a simple polyanion glass.



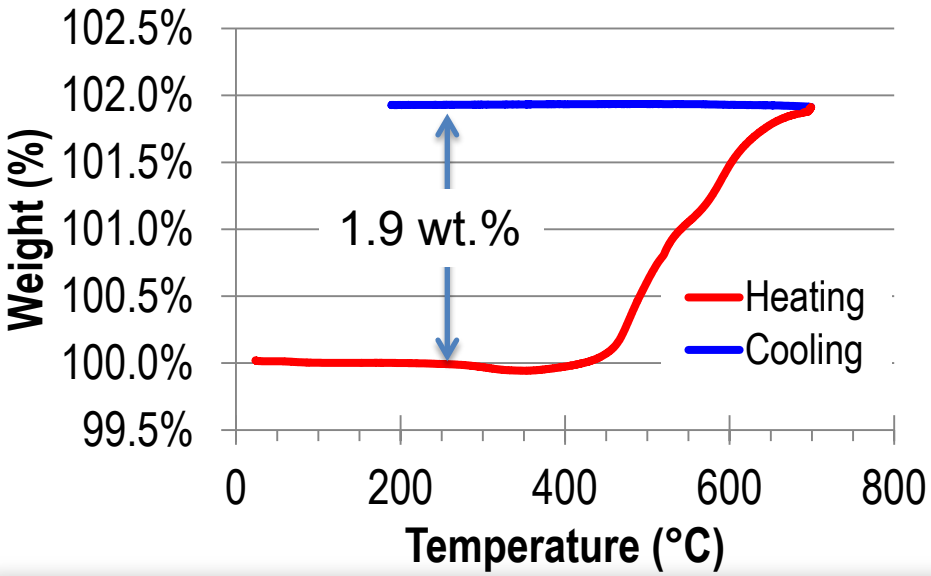
*Theoretical capacity assuming all Fe is Fe^{3+}.
**50% subst. has revised slurry recipe with more carbon black.

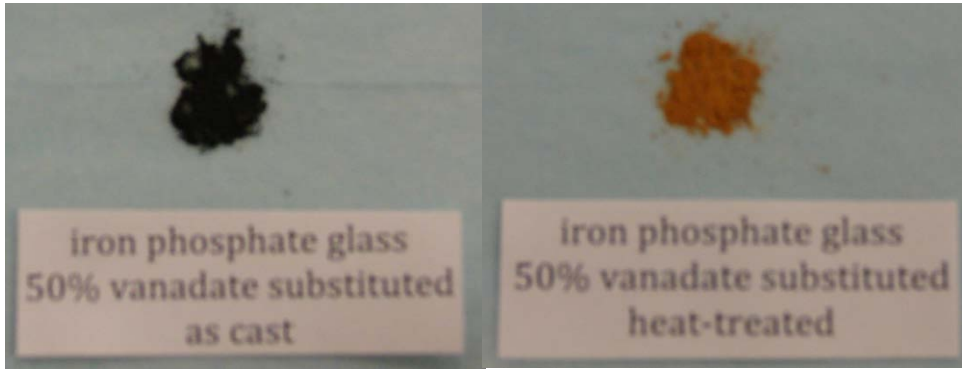
Potential use of thermal annealing for valence control

Technical Accomplishments

The transition metal anions in the glass must be in the correct valence to achieve theoretical capacity.

- The high temperature processing (~1300°C) of iron-bearing glasses causes a mixture of Fe^{3+} and Fe^{2+} anions.
- Thermal analysis (DTA/TGA) has indicated that a thermal anneal of iron-bearing glasses in air can convert Fe^{2+} anions to Fe^{3+}.





An oxygen gain of 1.9 wt.% would imply up to 48% of the iron as Fe^{2+} in the as-cast glass (some may be due to V valence).

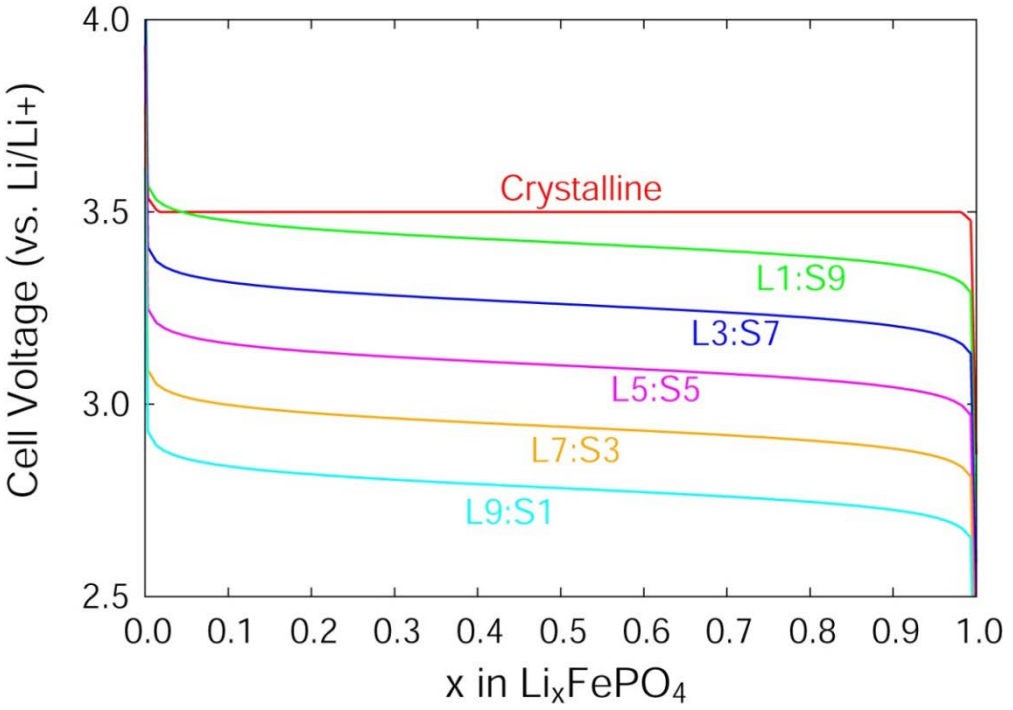
Computational thermodynamic modeling of glass cathodes

Technical Accomplishments

- Gibbs energy for the liquid phase in Li_xFePO_4 has been estimated from constituents to reproduce experiments.
- Glass model uses combined Gibbs energies for solid and liquid phases.

  (ex) L1:S9$\rightarrow 0.1G^{Liq}+0.9G^{Sol}$
- Experimental electrochemical data of polyanion glasses will help refine the modeling of glasses.

Baseline glass materials have been modeled with the CALPHAD approach to predict electrochemistry of Li_xFePO_4 glass.



Collaborations and Coordination with Other Institutions

- Glass processing collaborations at ORNL
  - Lynn Boatner, Joanne Ramey:
    thermal quench processing of novel glass materials
  - Pooran Joshi:
    glass processing using pulse thermal processing

- Planned collaborations with BATT program
  - Vince Battaglia (LBNL): benchmark testing in pouch cells
  - Brett Lucht (Univ. of Rhode Island): high voltage electrolytes
  - High energy phosphate glasses for potential sharing with collaborators this fiscal year

Upcoming Focus

Proposed Future Work

FY2013

- Establish the effect of glass annealing on transition metal valence.
  Achieving full theoretical capacity
- Pursue phosphate glasses of highest energy promise (Mn, Co, Ni).
  Reaching higher voltages & specific energies 30% greater than $LiFePO_4$
- Use models to predict behavior of future mixed polyanion glass candidates.
  Leading our processing efforts toward the most promising glass candidates
- Explore pulse thermal processing to produce glasses
  Enabling valence control and novel glass systems

FY2014

- Progress to borate and silicate glass systems.
  Seeking projected specific energies over 1000 mWh/g
- Guided by model predictions, explore promising novel glass systems.
  Searching beyond the initial proposed glass concepts
- Establish cycle life and optimize most promising glass candidates.
  Showing the potential to satisfy PHEV cycling and rate requirements

Alternative Processing

Proposed Future Work

- Pulse thermal processing for rapid heating/cooling of glass precursors is being evaluated for mixed polyanion glass production.
  - Collaboration with Pooran Joshi (ORNL)
  - Heating time as short as 3 μs ➔ limited valence change
  - Valence control may allow production of lithiated glasses in a fully discharged state.
  - Some glass systems are poorly suited for conventional high temperature glass processing, but may be suitable for pulse thermal processing. ➔ novel glasses with highly electronegative polyanions and increased redox potential (ex. sulfate glasses)

Summary

Relevance	• Mixed polyanion glass cathodes could overcome the problems in promising crystalline cathodes of poor conductivity and irreversible phase changes. • Potential for specific energy exceeding 1000 mAh/g
Approach	• Program structure: glass processing, modeling, glass characterization, cathode production, and electrochemical testing • Completed all FY12 milestones; On-schedule for FY13
Technical Accomplishments	• Demonstrated improvement in rate performance and specific capacity with mixed polyanion content • Produced computational model of the electrochemical performance of a polyanion glass
Future Work	• FY13: Phosphate glasses of highest energy promise (projected 30% greater specific energy than LFP) • FY14: Borate and silicate glass systems (projected specific energies up to over 1000 mWh/g)

Technical Back-Up Slides

Why glass?

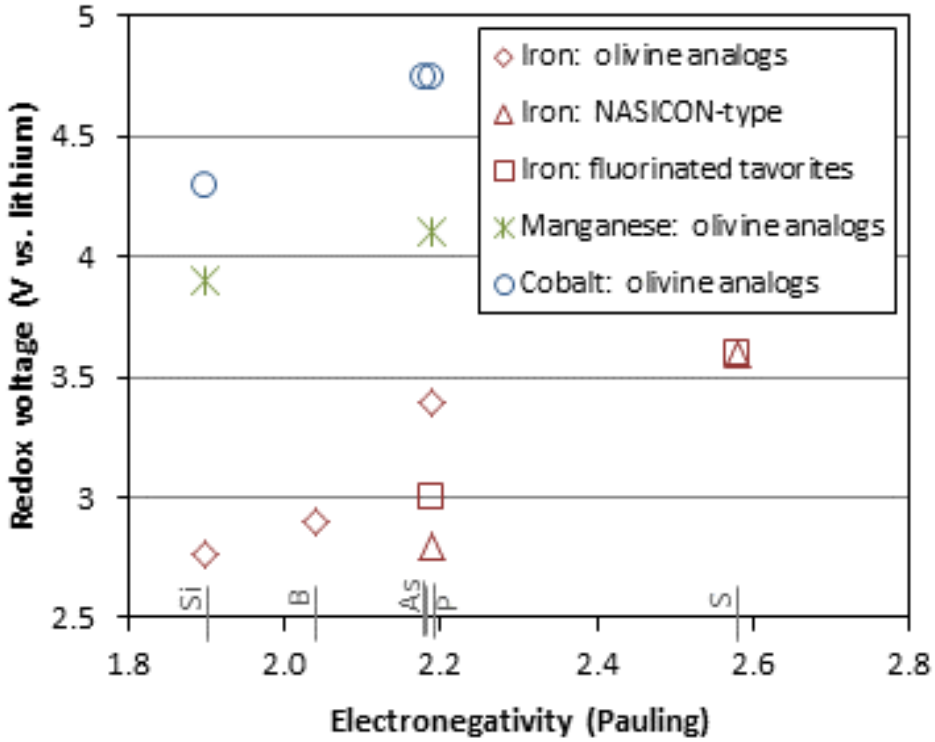
Tailored voltages

The redox voltage of polyanion cathodes is affected by:

- Transition metal cation (ex. Fe, Mn, Co)
- Inductive effect of the polyanion (ex. PO_4, BO_3, SiO_4)
- The framework structure

Crystalline polyanion cathodes cannot be tailored to obtain an optimal voltage due to limited number of stable compounds.

The polyanion content of glasses can be tailored in order to obtain a desired cell voltage.[1]



1. Isono M, et al., Journal of Power Sources, 195: 593-598, 2010.

Why glass?

Increased conductivity

A crystalline compound typically has a higher conductivity than an analogous glass.

However, mixed polyanion glasses can have higher electrical conductivities than similar crystalline polyanion frameworks.[1,2,3,4]

Material	Electrical conductivity
Lithium iron phosphate	~10^{-9}-10^{-10} S/cm
Iron phosphate glass	~10^{-10} S/cm
Iron phosphate glass – 30% vanadate substituted	~10^{-8} S/cm
Iron phosphate glass – 50% vanadate substituted	~10^{-6} S/cm

Improved conductivity has 2 advantages:

(1) high capacity at high currents

(2) enable promising, but failed cathode materials

1. Mogus-Milankovic M, et al., Journal of Non-Crystalline Solids, 345-6: 494-499, 2004.
2. Tanaka K, et al., Journal of Non-Crystalline Solids, 125: 264-271, 1990.
3. Shapaan M, et al., Physica B, 404: 2058-2064, 2009.
4. Santic B, et al., Journal of Non-Crystalline Solids, 296: 65-73, 2001.

Why glass?

No crystal structure changes

Several promising polyanion framework cathodes (such as $LiFeBO_3$,[1] $LiCoBO_3$,[1] Li_2MnSiO_4,[2] $LiCoSiO_4$[3]) have not cycled well due to crystal structure changes during cycling and/or low conductivities.

The disordered covalently-bonded polyanion structure of mixed polyanion glasses limits the ability of the structure to rearrange, so that excellent cycle life can be achieved in mixed polyanion glass materials analogous to these promising cathode materials that cycled poorly.

1. Legagneur V, et al., Solid State Ionics, 139: 37-46, 2001.
2. Domiko R, et al., Journal of Power Sources, 174: 457-461, 2007.
3. Lyness C, et al., Chemical Communications, 46: 4890-4892, 2007.

Examples of LBMP glass cathodes

Compared to LFP, mixed polyanion glass cathodes offer the potential of:

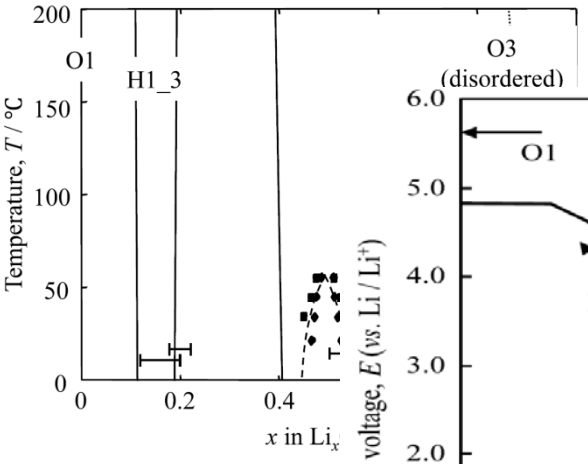
- increased specific energy
- higher capacity at high discharge rate

… and having the excellent safety performance & cycling of $LiFePO_4$.

Crystalline polyanion framework material			Potential LBMP glass			
Material	V	Theo. Cap.	Glass Composition	V	Theo. Cap. mAh/g	% inc. S.E.
$LiFePO_4$	3.4	170	70% $LiFePO_4$ / 30% $LiFeVO_4$	3.1	164	-11%
$LiMnPO_4$	4.1	171	70% $LiMnPO_4$ / 30% $LiMnVO_4$	4.0	165	13%
$LiMnBO_3$	4.0	222	70% $LiMnBO_3$ / 30% $LiMnVO_4$	3.9	195	31%
			85% $LiMnBO_3$ / 15% $Li_2Mn_2(MoO_4)_3$ (polyanion content 35% MoO_4)	4.0	160	11%
$LiCoBO_3$	4.5	215	60% $LiCoBO_3$ / 40% $LiCoVO_4$	4.3	182	36%
Li_2MnSiO_4	3.9	333 (166)	70% Li_2MnSiO_4 / 30% $LiMnVO_4$	3.8	275 (162)*	81% (7%)*
			85% Li_2MnSiO_4 /15% $Li_2Mn_2(MoO_4)_3$ (polyanion content 35% MoO_4)	3.9	236 (136)*	60% (-8%)*
Li_2CoSiO_4	4.3	163	70% Li_2CoSiO_4 / 30% $LiCoVO_4$	4.2	316	130%
			50% Li_2CoSiO_4 / 50% $LiCoVO_4$	4.2	310	123%

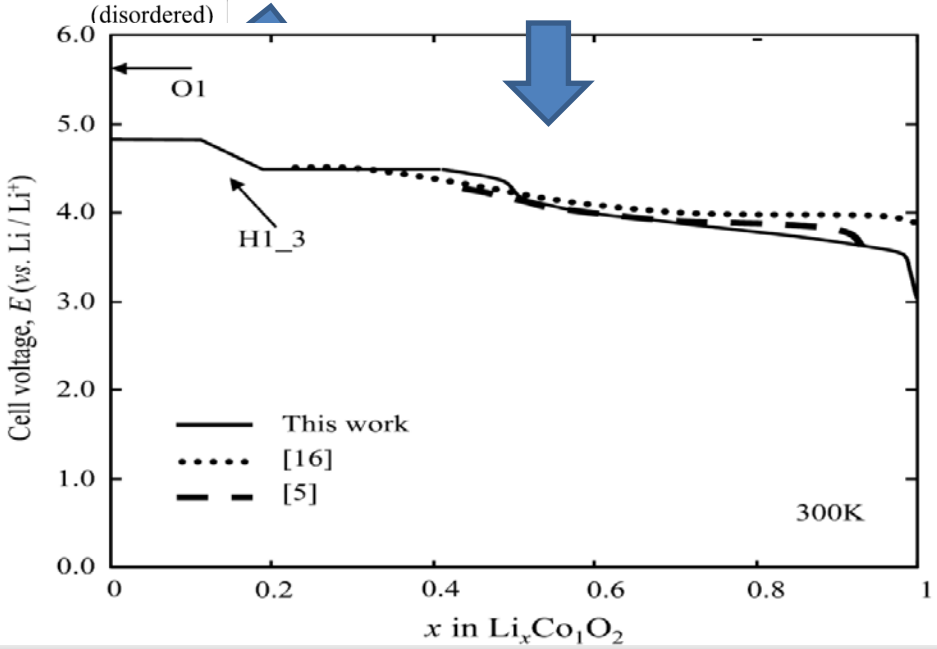
Computational Thermodynamic Modeling

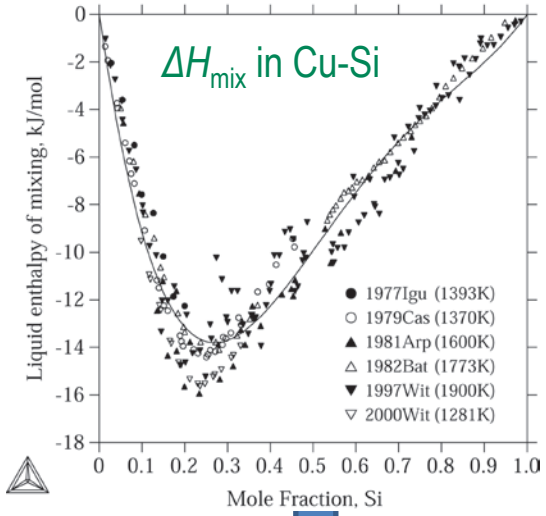
- CALPHAD (CALculation of PHAse Diagram) Approach
- Evaluate Gibbs energy of individual phases from experimental/theoretical data
- Thermochemical and phase equilibrium data
- Li-ion cell potentioal can be predicted from crystalline thermodynamic database by calculating μ_{Li}

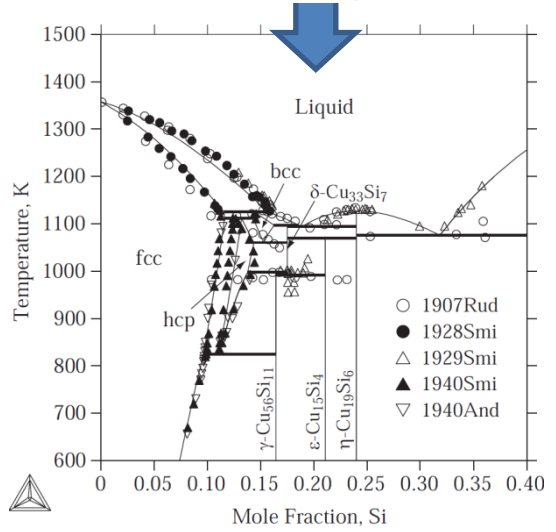


T. Abe and T. Koyama, *CALPHAD*, 35, 209–218 (2011)

Li/CoO_2 thermodynamic database







Shin et al., *CALPHAD*, 32(3), 520-526 (2008)